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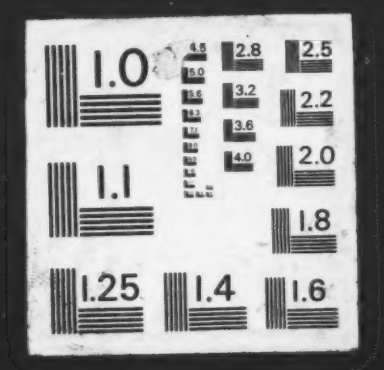

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POLYCHLORINATED BIPHENYLS IN THE SURFACE WATERS AND BOTTOM SEDIMENTS OF THE MAJOR DRAINAGE BASINS OF THE UNITED STATES

D. Steve Dennis, Ph.D*

Abstract

Data gathered from monitoring activities indicate the widespread occurrence of PCB's in surface waters and bottom sediments of the major drainage basins of the United States. A preliminary assessment of PCB levels shows median residue levels of the positive detections for the years 1971 to 1974 ranging between 0.1 to 3.0 µg/l for unfiltered water samples and from 1.2 to 160.0 µg/kg for bottom sediments. The highest levels were found in basins east of the Mississippi and bottom sediments may contain concentrations of PCB's many times higher than those in the overlying water.

INTRODUCTION

Within the past few years, particularly in the past year, polychlorinated biphenyls (PCB's) have been identified as a major contaminant of natural waters. PCB's in the hydrologic environment can originate from several sources including: (1) runoff from sewage sludges disposed of on land, (2) discharge of industrial and municipal wastes (this includes treated as well as untreated wastes), (3) accidental spills or improper waste disposal practices, and (4) formerly as ingredients of pesticides or as carriers for pesticides. Probably the largest amount of PCB's in the environment results from industrial and municipal discharges to inland and coastal waters (refs. 1–5).

Although much attention has been focused on estimating levels of PCB's in aquatic organisms, and the potential hazards involved, few data are available on the occurrence of PCB's in water and bottom sediments. The U.S. Department of Interior's Geological Survey and the U.S. Environmental Protection Agency's (EPA) Office of Pesticide Programs, Technical Services Division, through their National Water Monitoring Program for Pesticide Residues and various water-resource-assessment projects, are accumulating data which permit a preliminary assessment of PCB contamination of the Nation's drainage basins. The data presented here were gathered by the Geological Survey. They show the occurrence of PCB's (PCB mixtures predominately resemble Aroclor 1254) in whole water samples (i.e., water samples which are unfiltered) and in bottom sediments in the 17 major drainage basins of the United States and Puerto Rico (figure 1) for the years 1971 to 1974. All data were obtained from STORET, which is EPA's computerized information system that draws on both State and Federal agencies for parametric data relating to water quality.

Although there is not a nationwide program specifically designed to assess PCB levels in the aquatic environment, the present Geological Survey and EPA water monitoring programs are expanding and gradually increasing to more adequately determine PCB levels in the surface waters of the United States. These programs are also being designed to determine both national and regional trends in the concentration of PCB's.

METHODS AND PROCEDURES

Water samples were collected either by depth integration at the center of flow or by the equal-transit-rate method. In the latter method a standard suspended-sediment sampler, such as the US D-49 suspended-sediment sampler, was used to collect a velocity- and discharge-weighted sample. Samples were taken at a number of equally spaced verticals across a stream, depending on stream width (usually three sites were sampled across a stream). The transit rate of movement of the sampler from the water surface to the stream bed and back to the surface was the same at all verticals. Samples collected at each vertical were composited into a single sample intended to represent the entire flow across the stream.

Bottom sediments were sampled by collecting a series of cores across the stream bed using piston type or US BMH-60 or US BM-54 bed material samplers or a commercial core sampler. When a core sampler was used, cores were composited to form a representative sample of the stream bed (see refs. 5,6 for a description of sampling procedures).

Once the samples were collected, PCB residues were analyzed by the multiple-pesticide-residue methods for water, suspended sediment, and bottom sediment described by Goerlitz and Brown (ref. 7).

Basic identification of PCB residues was made by dual-column electron capture/gas-liquid chromatography and confirmed by gas-liquid chromatography or mass spectrometry. The amount of PCB's was determined by matching the peaks on the chromatogram with the nearest commercial formulation. The reported values are subject to some error because of the complexity of multiple peaks resulting from mixtures of PCB's in environmental samples.

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Figure 1. Map showing the major drainage basins in the United States and Puerto Rico.

Table 1. PCB's in whole water samples in the major drainage basins of the United States and Puerto Rico for 1971

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/l	Range of positive detections in µg/l
1. North Atlantic Slope	12	58.3	0.2	0.1 - 2.1
2. South Atlantic Slope and Eastern Gulf of Mexico	12	0	ND	ND
3. Ohio River	-	-	-	-
4. St. Lawrence River	15	26.7	0.3	0.1 - 0.5
5. Hudson Bay and Upper Mississippi River	-	-	-	-
6. Missouri River	1	0	ND	ND
7. Lower Mississippi	1	100.0	3.0	3.0
8. Western Gulf of Mexico	9	44.4	0.3	0.1 - 0.7
9. Colorado River	-	-	-	-
10. Great Basin	-	-	-	-
11. Pacific Slope Basins in California	-	-	-	-
12. Pacific Slope Basins in Washington	-	-	-	-
13. Snake River	-	-	-	-
14. Pacific Slope Basins in Oregon and Lower Columbia River	-	-	-	-
15. Alaska	-	-	-	-
16. Hawaii	-	-	-	-
17. Puerto Rico	-	-	-	-

Note: - = no samples; ND = not detected.

Table 2. PCB's in whole water samples in the major drainage basins of the United States and Puerto Rico for 1972

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/l	Range of positive detections in µg/l
1. North Atlantic Slope	112	17.0	0.1	0.1 - 0.3
2. South Atlantic Slope and Eastern Gulf of Mexico	122	0.8	ND	ND
3. Ohio River	10	20.0	0.2	0.1 - 0.2
4. St. Lawrence River	29	13.8	0.1	0.1 - 0.2
5. Hudson Bay and Upper Mississippi River	12	16.7	0.3	0.2 - 0.3
6. Missouri River	34	0	ND	ND
7. Lower Mississippi	39	2.6	0.1	0.1
8. Western Gulf of Mexico	93	8.6	0.3	0.1 - 2.6
9. Colorado River	24	0	ND	ND
10. Great Basin	9	0	ND	ND
11. Pacific Slope Basins in California	20	0	ND	ND
12. Pacific Slope Basins in Washington	14	0	ND	ND
13. Snake River	-	-	-	-
14. Pacific Slope Basins in Oregon and Lower Columbia River	3	0	ND	ND
15. Alaska	-	-	-	-
16. Hawaii	1	0	ND	ND
17. Puerto Rico	3	0	ND	ND

Note: - = no samples; ND = not detected.

Table 3. PCB's in whole water samples in the major drainage basins of the United States and Puerto Rico for 1973

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/l	Range of positive detections in µg/l
1. North Atlantic Slope	109	3.7	0.1	0.1
2. South Atlantic Slope and Eastern Gulf of Mexico	114	4.4	0.1	0.1 - 20.0
3. Ohio River	6	0	ND	ND
4. St. Lawrence River	31	3.2	0.1	0.1
5. Hudson Bay and Upper Mississippi River	30	10.0	0.2	0.1 - 0.4
6. Missouri River	95	0	ND	ND
7. Lower Mississippi	291	0.7	1.6	0.2 - 2.9
8. Western Gulf of Mexico	362	1.7	0.3	0.1 - 0.6
9. Colorado River	64	0	ND	ND
10. Great Basin	12	0	ND	ND
11. Pacific Slope Basins in California	73	0	ND	ND
12. Pacific Slope Basins in Washington	33	0	ND	ND
13. Snake River	2	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	9	0	ND	ND
15. Alaska	-	-	-	-
16. Hawaii	1	0	ND	ND
17. Puerto Rico	37	0	ND	ND

Note: - = no samples; ND = not detected.

Table 4. PCB's in whole water samples in the major drainage basins of the United States and Puerto Rico for 1974

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/l	Range of positive detections in µg/l
1. North Atlantic Slope	51	2.0	0.1	0.1
2. South Atlantic Slope and Eastern Gulf of Mexico	151	0	ND	ND
3. Ohio River	24	0	ND	ND
4. St. Lawrence River	38	0	ND	ND
5. Hudson Bay and Upper Mississippi River	33	0	ND	ND
6. Missouri River	28	0	ND	ND
7. Lower Mississippi	269	2.6	0.1	0.1 - 0.2
8. Western Gulf of Mexico	325	1.2	0.3	0.2 - 0.7
9. Colorado River	52	0	ND	ND
10. Great Basin	12	0	ND	ND
11. Pacific Slope Basins in California	74	2.7	0.1	0.1
12. Pacific Slope Basins in Washington	13	7.7	0.1	0.1
13. Snake River	11	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	8	0	ND	ND
15. Alaska	-	-	-	-
16. Hawaii	1	0	ND	ND
17. Puerto Rico	68	1.5	0.8	0.8

Note: - = no samples; ND = not detected.

Table 5. PCB's in bottom sediments in the major drainage basin of the United States and Puerto Rico for 1971

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/kg	Range of positive detections in µg/kg
1. North Atlantic Slope	3	100.0	50.0	10.0 - 100.0
2. South Atlantic Slope and Eastern Gulf of Mexico	19	63.2	64.5	10.0 - 200.0
3. Ohio River	1	100.0	8.8	8.8
4. St. Lawrence River	1	100.0	10.0	10.0
5. Hudson Bay and Upper Mississippi River	-	-	-	-
6. Missouri River	2	100.0	1.2	0.3 - 2.0
7. Lower Mississippi	4	100.0	30.0	10.0 - 80.0
8. Western Gulf of Mexico	20	100.0	10.0	2.0 - 290.0
9. Colorado River	-	-	-	-
10. Great Basin	-	-	-	-
11. Pacific Slope Basins in California	-	-	-	-
12. Pacific Slope Basins in Washington	-	-	-	-
13. Snake River	-	-	-	-
14. Pacific Slope Basins in Oregon and Lower Columbia River	-	-	-	-
15. Alaska	-	-	-	-
16. Hawaii	-	-	-	-
17. Puerto Rico	-	-	-	-

Note: - = no samples; ND = not detected.

Table 6. PCB's in bottom sediments in the major drainage basins of the United States and Puerto Rico for 1972

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/kg	Range of positive detections in µg/kg
1. North Atlantic Slope	56	57.1	10.0	5.0 - 800.00
2. South Atlantic Slope and Eastern Gulf of Mexico	101	32.7	30.0	5.0 - 500.00
3. Ohio River	-	-	-	-
4. St. Lawrence River	10	90.0	20.0	2.0 - 800.0
5. Hudson Bay and Upper Mississippi River	3	0	ND	ND
6. Missouri River	22	81.8	2.0	2.0
7. Lower Mississippi	25	48.0	2.0	2.0 - 2400.0
8. Western Gulf of Mexico	66	43.9	4.0	2.0 - 250.0
9. Colorado River	7	71.4	2.0	2.0
10. Great Basin	9	66.7	2.0	2.0
11. Pacific Slope Basins in California	6	83.3	20.0	2.0 - 190.0
12. Pacific Slope Basins in Washington	9	44.4	2.0	2.0
13. Snake River	1	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	1	100.0	2.0	2.0
15. Alaska	-	-	-	-
16. Hawaii	1	0	ND	ND
17. Puerto Rico	-	-	-	-

Note: - = no samples; ND = not detected.

Table 7. PCB's in bottom sediments in the major drainage basins of the United States and Puerto Rico for 1973

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/kg	Range of positive detections in µg/kg
1. North Atlantic Slope	58	70.7	10.0	4.0 - 4000.0
2. South Atlantic Slope and Eastern Gulf of Mexico	123	48.8	10.0	5.0 - 600.0
3. Ohio River	4	25.0	20.0	20.0
4. St. Lawrence River	24	91.7	20.0	5.0 -13000.0
5. Hudson Bay and Upper Mississippi River	14	0	ND	ND
6. Missouri River	17	0	ND	ND
7. Lower Mississippi	57	1.8	20.0	20.0
8. Western Gulf of Mexico	188	3.7	50.0	14.0 - 180.0
9. Colorado River	4	0	ND	ND
10. Great Basin	7	0	ND	ND
11. Pacific Slope Basins in California	14	0	ND	ND
12. Pacific Slope Basins in Washington	12	0	ND	ND
13. Snake River	1	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	-	-	-	-
15. Alaska	2	0	ND	ND
16. Hawaii	1	0	ND	ND
17. Puerto Rico	6	16.7	5.0	5.0

Note: - = no samples; ND = not detected.

Table 8. PCB's in bottom sediments in the major drainage basins of the United States and Puerto Rico for 1974

Drainage basins	Sample size	% of positive detections	Median of positive detections in µg/kg	Range of positive detections in µg/kg
1. North Atlantic Slope	99	56.6	31.0	2.0 - 800.0
2. South Atlantic Slope and Eastern Gulf of Mexico	171	25.7	11.0	2.0 - 530.0
3. Ohio River	6	33.3	35.0	9.0 - 61.0
4. St. Lawrence River	40	60.0	20.0	3.0 - 700.0
5. Hudson Bay and Upper Mississippi River	26	0	ND	ND
6. Missouri River	5	0	ND	ND
7. Lower Mississippi	81	9.9	10.5	1.0 - 39.0
8. Western Gulf of Mexico	157	21.7	27.0	2.0 - 330.0
9. Colorado River	3	0	ND	ND
10. Great Basin	4	0	ND	ND
11. Pacific Slope Basins in California	26	11.5	2.0	2.0 - 65.0
12. Pacific Slope Basins in Washington	5	0	ND	ND
13. Snake River	4	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	1	0	ND	ND
15. Alaska	-	-	-	-
16. Hawaii	-	-	-	-
17. Puerto Rico	18	27.2	160.0	10.0 - 640.0

Note: - = no samples; ND = not detected.

RESULTS

Tables 1 through 8 present the PCB residue data by year for water and bottom sediments. For each year the following is given: number of samples, percent of positive detections, median of positive detections, and maximum of positive detections in µg/l for water and µg/kg for bottom sediments (one µg/l and one µg/kg are roughly equivalent to one ppb).

Not all drainage basins had detectable levels of PCB's in both water and bottom sediments. However, it should be noted that this may be in part due to the location of sampling stations within drainage basins and/or the small number of samples within drainage basins.

Median residue levels of the positive detections in whole water samples ranged from 0.2 to 3.0 µg/l, 0.1 to 0.3 µg/l, 0.1 to 1.6 µg/l, and 0.1 to 0.8 for all drainage basins for 1971, 1972, 1973, and 1974, respectively (tables 1 to 4). For both these data and the data for each basin there is no indication of an increase in PCB levels and in many instances the levels decreased. The highest PCB level was found in the South Atlantic Slope and Eastern Gulf of Mexico basin and in general, the highest levels were found in basins east of the Mississippi. One might speculate that this is due to the presence of certain industries in the eastern United States.

Bottom sediments showed a pattern similar to that of water with the highest PCB residue levels occurring in the eastern United States (table 5 to 8). Median residue levels of the positive detections for all basins ranged from 1.2 to 64.5 µg/kg, 2.0 to 30.0 µ/kg, 5.0 to 50.0 µg/kg, and 2.0 to 160.0 µg/kg for 1971, 1972, 1973, and 1974, respectively. The data indicate that, as with the whole water samples, the levels decreased in some basins. However, it appears as if PCB's are more persistent in bottom sediments.

DISCUSSION

The data which I have presented here indicate that PCB's are widespread in the surface waters and bottom sediments of the Nation. Crump-Wiesner et al. (ref. 9) also found PCB's to have a ubiquitous occurrence and distribution in surface water, ground water, and bottom sediments. According to Veith and Lee (ref. 8) ". . . the chlorinated biphenyls may be one of the more widespread. . ." environmental contaminants.

It is well documented that bottom sediments may contain concentrations of pesticide residues many times higher than the overlying water (refs. 10-13). The data presented here and previously published data (refs. 1,4,9,14) indicate that a similar relationship holds true for PCB's. Even in drainage basins, where PCB's were not detected in water samples such as the Missouri River, they were present in bottom sediments. It is assumed that this is due to the low water solubility and high specific gravity of PCB's (ref. 14). According to Nisbet and Sarofim (ref. 14), ". . . it is expected that most of the PCBs discharged into the environment will be resting as sludges or adsorbed in the sediment at the bottom of rivers or lakes near their point of discharge, and that transport in streams will be primarily by means of waterborne particles."

Finally, it is important to note that although PCB's are found in water and bottom sediments, this information must be related to the entire aquatic environment before the data can be adequately evaluated. This is because (1) PCB's in solution and sorbed on organic and inorganic particles are available for introduction into food chains, (2) PCB's are accumulated in the tissues of animals which are exposed to water and bottom sediments containing PCB's, (3) biological magnification may occur in food chains, and (4) all components in an aquatic ecosystem are interrelated.

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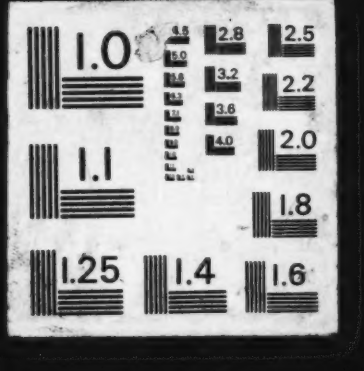

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Chlorinated Hydrocarbon Pesticides and Mercury in Coastal Biota, Puerto Rico and the U.S. Virgin Islands—1972-74[1]

Robert J. Reimold[2]

ABSTRACT

Baseline levels of mercury and chlorinated hydrocarbons were determined for Caribbean coastal biota as part of the U.S. Environmental Protection Agency estuarine monitoring program. Forty-one percent of the 150 environmental samples taken had significant levels of these compounds.

Concentrations of chlorinated hydrocarbons suggest spatial and temporal variations within the plant or animal. In some cases residues in biota could be related to the land-use practices in the sampled watershed.

Introduction

The presence of chlorinated hydrocarbons in continental U.S. marine and estuarine organisms has been routinely monitored since 1965 (*1, 2*). There is, however, a paucity of data concerning concentrations of these chlorinated hydrocarbons in estuarine and marine fauna and flora from the Caribbean (*3*).

As part of the estuarine monitoring program of the U.S. Environmental Protection Agency (EPA), a biannual survey of selected Caribbean islands was initiated in October 1972. The purpose of this paper is to report baseline concentrations including negative results in selected environmental samples collected from U.S. territories in the Caribbean.

Methods

The study area includes Puerto Rico and the U.S. Virgin Islands of St. John, St. Thomas, and St. Croix. Collection locations for each of the four island areas are identified in Figures 1 and 2. At each location, samples were collected within 1 km of the edge of shore. Sites were selected in watersheds which respond quickly to rainfall and produce runoff which might contribute pollutants to coastal biota.

Samples were collected by seine, trap, hook and line, or by hand during fall 1972, spring 1973, fall 1973, and spring 1974. They were immediately placed on ice in aluminum foil packets. Within 4 hours of collection, samples were processed for analysis according to previously developed techniques (*4,5*). Operating parameters of the gas-liquid chromatographic (GLC) techniques were:

Column:	glass, 5 ft by 18 in., packed with 3 percent DC-200 on 80/100 mesh Gas-Chrom Q
Temperatures:	Oven 190° C Injector 210° C Detector 210° C
Carrier Gas:	Prepurified nitrogen at a flow rate of 40 ml/min. Three columns of different polarity were used for confirmation.

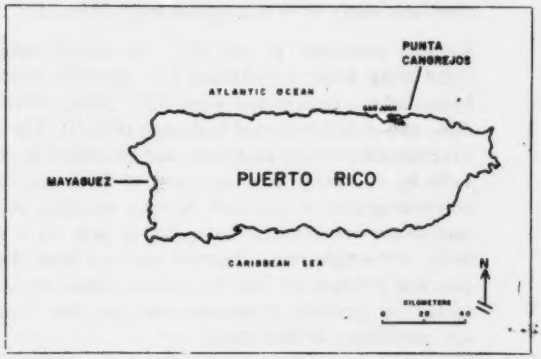

FIGURE 1. *Collection sites for coastal biota, Puerto Rico*

[1] Contribution No. 286, Marine Institute, University of Georgia, Sapelo Island, Ga. 31327. Project funded in part by U.S. EPA Contract 68-02-1254.

[2] Marine Resources Extension Center, University of Georgia, P.O. Box 517, Brunswick, Ga. 31520.

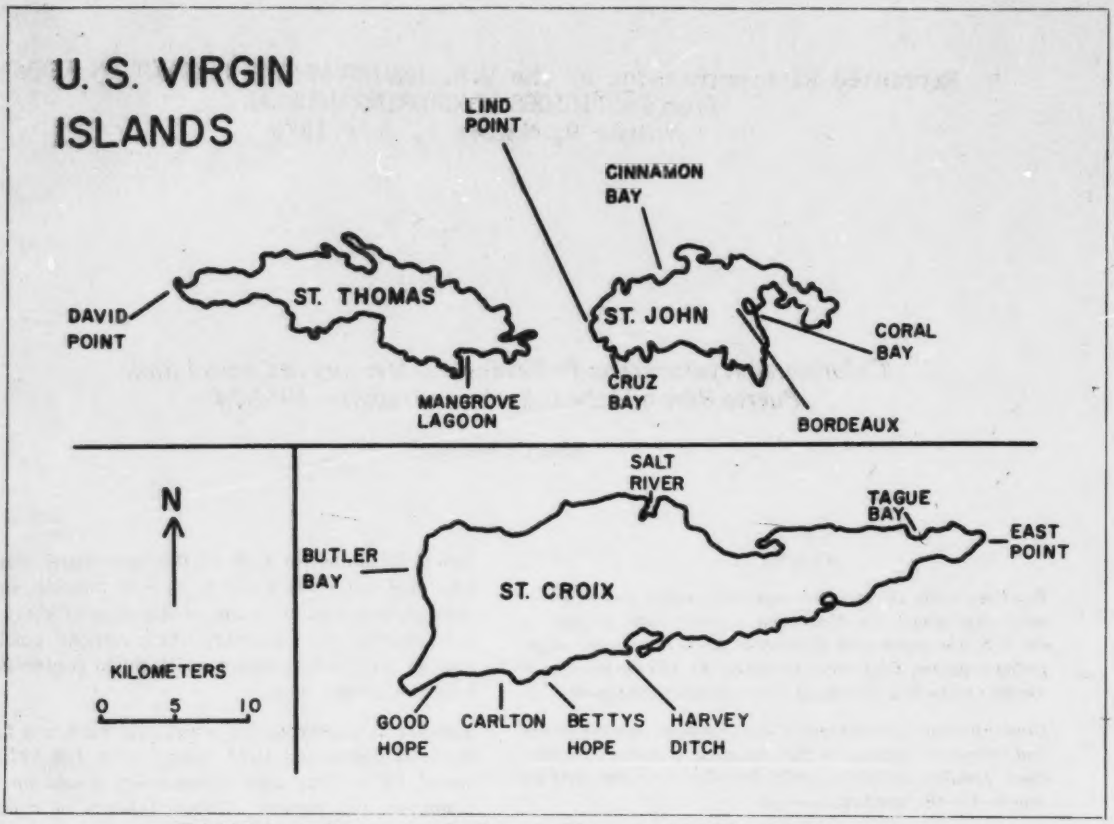

FIGURE 2. *Collection sites: St. Croix, St. Thomas, and St. John, U.S. Virgin Islands*

Analyses were performed by the EPA Pesticide Monitoring Laboratory, Bay St. Louis, Miss., and by the Marine Institute Laboratory, University of Georgia, Sapelo Island. In an earlier monitoring program for chlorinated hydrocarbon pesticides, the two laboratories synchronized methodologies and analyzed split samples. Results from this study were not significantly different.

Samples processed by the EPA laboratory were analyzed using Butler's technique (*2*). Specific chlorinated hydrocarbons determined were DDT, DDE, TDE, dieldrin, and polychlorinated biphenyls (PCB's). The PCB's were separated from pesticides and identified as Aroclor 1254 by matching chromatograms of field samples with chromatograms of standard Aroclor samples. All concentrations are reported as μg/kg or ppb on a whole-body, wet-weight basis. Relative recovery from the samples was between 85 and 90 percent. Data are not corrected for recovery. Concentrations less than 5 ppb are not considered in this study.

All analyses for mercury were conducted by the EPA laboratory using the techniques of Uthe et al. (*6*) and Brandenberger and Bader (*7,8*). These results are also expressed in μg/kg or ppb on a whole-body, wet-weight basis. Mercury concentrations less than 0.02 μg/kg are not considered.

Results

Of 150 environmental samples collected and analyzed, 41 percent had significant concentrations (> 5 ppb) of mercury or chlorinated hydrocarbons (Table 1). Table 2 lists scientific names of the biota and summarizes sample collection data.

Low concentrations of dieldrin were found in red mangrove leaves collected from St. Croix and St. John. There were also very low concentrations of dieldrin in a Nassau grouper and a soldier crab, both from St. John. Occurrence of dieldrin in St. John samples from the Coral Bay coincides with the presence of dieldrin in well and cistern water from a church at the bay (*9*). Cistern water sampled in 1970 contained 0.01 ppb dieldrin.

TABLE 1. *Chlorinated hydrocarbon concentrations in biota, U.S. Virgin Islands and Puerto Rico, 1972-74*

Date	Location	Common Name	Residues, ppb					
			Dieldrin	DDT	DDE	TDE	PCB's	Mercury
Fall '72	Mayaguez PR	Snook		157			162	
Spring '73	Mayaguez PR	Great barracuda		69	103			968
Spring '73	Mayaguez PR	Red drum						114
Fall '73	Mayaguez PR	Bluestriped grunt						70
Spring '74	Mayaguez PR	Yellowfin mojarra					399	
Spring '74	Mayaguez PR	Barbu					157	824
Fall '72	Punta Cangrejos PR	West Indian sardine		39		25	201	
Spring '73	Punta Cangrejos PR	West Indian sardine					416	271
Spring '73	Punta Cangrejos PR	Atlantic spadefish					240	194
Spring '73	Punta Cangrejos PR	Red mangrove						40
Spring '73	Punta Cangrejos PR	Great barracuda		69	103			968
Fall '73	Punta Cangrejos PR	Yellowfin mojarra						87
Spring '74	Punta Cangrejos PR	Striped mullet					579	
Spring '74	Punta Cangrejos PR	Silver jenny					89	
Spring '74	Punta Cangrejos PR	Red mangrove					68	80
Spring '74	Punta Cangrejos PR	Fiddler crab		<10	12	<10		
Fall '72	David Point STT	Red grouper					133	
Spring '73	David Point STT	Queen triggerfish						400
Spring '73	David Point STT	Red snapper						736
Fall '73	David Point STT	Queen triggerfish						822
Fall '73	David Point STT	Rock hind						290
Spring '74	David Point STT	Rock hind						304
Spring '74	David Point STT	Gray snapper						700
Spring '74	Mangrove Lagoon STT	Red mangrove					64	20
Fall '72	Cruz Bay STJ	Soldier crab		36	44	14		
Fall '72	Cruz Bay STJ	Red mangrove					129	
Fall '73	Cruz Bay STJ	Rock hind						40
Fall '72	Cinnamon Bay STJ	Mongoose (liver only)		22	47	11		
Fall '72	Coral Bay STJ	Soldier crab		43	132	14		
Fall '72	Coral Bay STJ	Red mangrove	21					
Fall '72	Coral Bay STJ	Turtle grass					40	
Fall '72	Coral Bay STJ	Nassau grouper	<10					
Spring '73	Coral Bay STJ	West Indian sardine					719	
Spring '73	Coral Bay STJ	Mangrove oysters						58
Spring '73	Coral Bay STJ	Schoolmaster						155
Spring '73	Coral Bay STJ	Porcupine fish						78
Fall '73	Coral Bay STJ	Red mangrove						50
Spring '74	Coral Bay STJ	Mangrove oysters					110	
Fall '73	Bordeaux STJ	Soldier crab	<10	30	112			
Fall '73	Bordeaux STJ	Soldier crab		758	17508			
Fall '73	Lind Point STJ	Soldier crab			21			
Fall '72	East End Point STX	Jewfish					495	
Fall '73	East End Point STX	Yellowtail snapper						83
Fall '73	East End Point STX	Ocean surgeon						25
Fall '73	East End Point STX	Queen triggerfish						75
Fall '72	Harvey Ditch STX	Red mangrove					181	
Fall '72	Harvey Ditch STX	Red mangrove					181	
Spring '73	Harvey Ditch STX	Red mangrove						38
Spring '74	Harvey Ditch STX	Striped mullet					809	
Spring '74	Harvey Ditch STX	French grunt					467	
Spring '74	Harvey Ditch STX	Spotted pink shrimp					4630	
Spring '74	Harvey Ditch STX	Fiddler crabs	<10				8624	
Spring '74	Harvey Ditch STX	Striped mullet					5391	
Fall '72	Bettys Hope STX	Red mangrove					132	
Fall '72	Bettys Hope STX	Checkered puffer					1817	
Fall '73	Carleton STX	Red mangrove					61	
Spring '73	Carleton STX	Red mangrove	11					
Fall '72	Good Hope STX	Fish doctor					166	
Fall '72	Butler Bay STX	Great barracuda					129	
Spring '73	Salt River STX	Mangrove oysters						39
Spring '73	Tague Bay STX	Great barracuda						271

NOTE: All residues are given on a whole-fish, wet-weight basis.
PR = Puerto Rico, STJ = St. John, STT = St. Thomas, STX = St. Croix.
Blank spaces indicate no residues detected.

DDT and DDE were found in mongoose liver collected from Cinnamon Bay, St. John, and soldier crabs collected at Coral Bay and nearby Bordeaux on St. John. Earlier studies of the cistern water and sediments at these sites did not reveal DDT or DDE (*9*), although they reported 0.14 ppm DDE in sediment of a cistern at Coral Bay.

DDT and DDE were found in East Indian sardines, snook, and great barracuda from Mayaquez, P.R. In the great barracuda, there were 69 μg/kg DDT and 103 μg/kg DDE on a whole-fish basis. Giam et al. (*3*) sampled great barracuda east of the Yucatan peninsula and detected 8 μg/kg DDT in the muscle and 42 μg/kg DDT in the liver.

TDE was found only in soldier crabs (14 μg/kg) and mongoose liver (11 μg/kg) from Cruz, Coral, and Cinnamon Bays, St. John. Earlier research efforts (*9*) did not reveal TDE at these sites.

Aroclor 1254, the only PCB compound identified, was found in West Indian sardines collected from Mayaguez,

P.R. (201 μg/kg), Punta Cangrejos, P.R. (416 μg/kg), and Coral Bay, St. John (719 μg/kg). This compound also appeared in red mangrove leaves from Cruz Bay, St. John (129 μg/kg); and from Harvey Ditch (181 μg/kg), Bettys Hope (132 μg/kg), and Carleton (61 μg/kg), all in St. Croix. Aroclor 1254 was also detected in several other fish (Table 1) including a great barracuda from Butler Bay, St. Croix (129 μg/kg), and striped mullet (5,391 μg/kg) and fiddler crabs (8,624 μg/kg) from Harvey Ditch, St. Croix. This is a considerably greater concentration of Aroclor 1254 than that reported in a great barracuda collected by Giam et al. (*3*), which had 9 μg/kg in the muscle and 57 μg/kg in the liver.

TABLE 2. *Genera, species, and common names of biota sampled, U.S. Virgin Islands and Puerto Rico, fall 1972—spring 1974*

SPECIES	PR	STJ	STT	STX
PLANTS				
Red mangrove (*Rhizophora mangle*)	X	X	X	X
Turtle grass (*Thalassia testudinum*)		X		
INVERTEBRATES				
Spotted pink shrimp (*Penaeus brasiliensis*)				X
Fiddler crab (*Uca pugilator*)	X			X
Soldier crab (*Coenobita clypeatus*)		X		
Pacific oysters[1] (*Crassostrea gigas*)				X
Mangrove oysters (*Crassostrea rhizophorae*)		X		X
Scallops[1] (*Argopecten irradians*)				X
FISH				
Ocean surgeon (*Acanthurus bahianus*)				X
Spotted eagle ray (*Aetobatus narinari*)				X
Queen triggerfish (*Balistes vetula*)			X	X
Bar jack (*Caranx ruber*)				X
Snook (*Centropomus undecimalis*)	X			
Atlantic spadefish (*Chaetodipterus faber*)	X			
Banded butterflyfish (*Chaetodon striatus*)				X
Porcupinefish (*Diodon hystrix*)		X		
Rock hind (*Epinephelus adscensionis*)	X	X	X	X
Jewfish (*Epinephelus itajara*)				X
Red grouper (*Epinephelus morio*)			X	
Nassau grouper (*Epinephelus striatus*)			X	X
Silver jenny (*Eucinostomus gula*)	X			
Yellowfin mojarra (*Gerres cinereus*)	X			X
Fish doctor (*Gymnelis viridis*)				X
Margate (*Haemulon album*)				X
French grunt (*Haemulon flavolineatum*)				X
White grunt (*Haemulon plumieri*)				X
Bluestriped grunt (*Haemulon sciurus*)	X	X		
Schoolmaster (*Lutjanus apodus*)	X	X		X
Red snapper (*Lutjanus campechanus*)			X	
Sand tilefish (*Malacanthus plumieri*)				X
Striped mullet (*Mugil cephalus*)	X			X
White mullet (*Mugil curema*)	X			
Yellowtail snapper (*Ocyurus chrysurus*)				X
Barbu (*Polydactylus virginicus*)	X			
Spotted goatfish (*Pseudupeneus maculatus*)		X		
West Indian sardine (*Sardinella sardina*)	X			
Striped parrotfish (*Scarus croicensis*)	X			
Red drum (*Sciaenops ocellata*)	X			
Redtail parrotfish (*Sparisoma chrysopterum*)				X
Stoplight parrotfish (*Sparisoma viride*)		X	X	X
Checkered puffer (*Sphoeroides testudineus*)				X
Great barracuda (*Sphyraena barracuda*)	X			X
MAMMALS				
Mongoose (*Herpestes javanicus*)				X

NOTE: PR = Puerto Rico, STT = St. Thomas, STJ = St. John, STX = St. Croix.

[1] Sample obtained from artificial upwelling mariculture project, Lamont-Doherty Geological Observatory, Columbia University.

The highest concentration of mercury, 968 μg/kg, was found in a great barracuda collected near Mayaguez, P.R., in spring 1973. It was also detected in the red snapper (400 μg/kg) collected at David Point, St. Thomas. Mercury also occurred in the red mangrove from Punta Cangrejos, P.R. (40 μg/kg) and from Harvey Ditch, St. Croix (38 μg/kg); and in other components low in the food chain, such as mangrove oysters from Coral Bay, St. John (58 μg/kg), and from Salt River, St. Croix (39 μg/kg).

Discussion

The author's findings supplement information recently published by Giam et al. (*3*) and Lenon et al. (*9*). In all three studies, concentrations of chlorinated hydrocarbons suggest spatial and temporal variation within the same plant or animal.

In some instances, residues in the biota could be related to the land-use practices in the watershed. At Coral Bay, St. John, the Virgin Islands Department of Health had employed both DDT and dieldrin in an insect control program. Lenon et al. (*9*) reported both DDT and dieldrin in cistern water at Coral Bay. As shown in Table 1 of the present study, dieldrin and DDT were found in measurable concentrations in fauna collected from Coral Bay.

In another instance illustrated in Table 1 and Figure 2, Aroclor 1254 was found in red mangroves on the south side of St. Croix. Residues in samples collected westward along the ocean shore during fall 1972 declined from the first measured concentration, 181 μg/kg at Harvey Ditch, to 132 μg/kg at Bettys Hope and 61 μg/kg at Carleton. By spring 1974, Aroclor 1254 had trophically magnified to levels of 8,624 μg/kg in the fiddler crabs and 5,391 μg/kg in striped mullet, both potential detrivores. The source of this PCB compound is not known. One might speculate that it is local, considering that residues are found at such low trophic levels in the primary producers and detrivores.

It is not yet possible to determine whether the detected measured pollutants are increasing, decreasing, or maintaining status quo. Data in this study do establish baseline conditions for future comparisons in these relatively uncontaminated areas of Puerto Rico and the U.S. Virgin Islands.

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PB 276 315

PCB's IN AGRICULTURAL AND URBAN SOIL

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Abstract

Polychlorinated biphenyls in soil have been monitored since 1972 as part of the National Soils Monitoring Program, originally established to measure pesticide residue levels in agricultural soils, raw agricultural commodities, and urban soils across the Nation. The PCB's are monitored as part of this program because of their chemical similarity to certain chlorinated pesticides.

The PCB's have rarely been detected in agricultural soils of the United States. Only 0.1 percent of the soil samples collected in the National Soils Monitoring Program for 1972 contained detectable PCB levels. However, detectable levels of PCB's occur more frequently in urban soils. Of the 19 metropolitan areas sampled since 1971, 12 of the cities, or 63 percent showed detectable PCB levels. The most commonly encountered PCB was Aroclor 1254, which was identified in approximately 40 percent of the positive samples, while Aroclor 1260 was prevalent in about 20 percent of the positive samples. In the remaining 40 percent of the positive samples, no identification was made of the specific Aroclor. The occurrence of these compounds appears to be more prevalent in the "urban" portion (within the city limits) than in the "suburban" portion (remainder) of these metropolitan areas.

INTRODUCTION

The occurrence of polychlorinated biphenyls (PCB's) in environmental media has been known and well-documented for several years; it is only recently that the magnitude of the contamination has created widespread concern.

These compounds have been monitored in agricultural and urban soils since 1972 as part of the National Soils Monitoring Program. This program was established to measure pesticide residue levels in agricultural soils, raw agricultural commodities, and urban soils across the Nation. It was initiated by the U.S. Department of Agriculture and is now operated by the U.S. Environmental Protection Agency. The PCB's are monitored as part of this program because of their chemical similarity to certain chlorinated pesticides.

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SAMPLING PROCEDURES

For cropland sampling, 50 cores 5.1 x 7.6 cm in size were collected over an evenly spaced 5 x 10 grid on each 4-hectare site (ref. 1). In urban sampling, this procedure was modified to collect 16 cores on a 4 x 4 grid over a 225-m^2 plot (15 x 15 m) (ref. 2). Field processing was similar for both types of samples; the cores were composited, thoroughly mixed, and sieved through a 6.3-mm mesh, and a 2-l subsample was sent to the EPA Technical Services Division's Pesticide Monitoring Laboratory in Bay St. Louis, Mississippi, for chemical analysis.

ANALYTICAL PROCEDURES

Sample Preparation

A 300-g subsample was dampened with water and extracted with 600 ml of 3:1 hexane:isopropanol solvent. The isopropanol was removed by three distilled water washes and the hexane extract was dried through anhydrous sodium sulfate and stored at low temperature for subsequent gas-liquid chromatographic analysis.

Gas-Liquid Chromatography

Analyses were performed on gas chromatographs equipped with tritium foil electron affinity detectors. A multiple system of polar and nonpolar columns was utilized for identification and confirmation. Instrument parameters were as follows:

Columns:

Glass, 6 mm o.d. x 4 mm i.d., 183-cm long, packed with one of the following: 9% QF-1 on 100/120-mesh Gas-Chrom Q; 3% DC-200 on 100/120-mesh Gas-Chrom Q; or 1.5% OV-17/1.95% QF-1 on 100/120-mesh Sepulcoport.

Carrier Gases:

5% methane-argon at a flow rate of 80 ml/min; prepurified nitrogen at a flow rate of 80 ml/min.

Temperatures:

Detector	200°C
Injection port	250°C
Column QF-1	166°C
Column DC-200	170°–175°C
Mixed column	185°–190°C.

Sensitivity or minimum detection levels were 0.05 to 0.1 ppm. The average recovery rate in soil was 90 to 110 percent.

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DISCUSSION

Agricultural Soils

PCB's have rarely been detected in the Nation's agricultural soils. Of the 1,556 soil samples collected in 1972 as part of the National Soils Monitoring Program, only 2 samples or 0.1 percent contained detectable levels of PCB's.

Urban Soils

Detectable levels of PCB's occur more frequently in urban soils than in agricultural soils. Of the 19 metropolitan areas sampled since 1971, 12 of the cities, or 63 percent showed detectable levels of PCB's. Corresponding data are presented in tables 1-4. The most commonly encountered PCB was Aroclor 1254, which was identified in 39 percent of the positive samples, while Aroclor 1260 was prevalent in 21 percent of the positive samples. Although no attempt was made to identify the specific Aroclor in 39 percent of the positive samples, it is likely that a majority contained Aroclor 1254.

All sites sampled within a metropolitan area were classified into two of four categories. First, sites were identified as either "lawn" or "waste," to indicate whether or not they seemed likely to receive regular maintenance. Secondly, each site was classified as urban if it was within the city limits, and suburban if it was located in the remainder of the metropolitan area.

When the positive sites in the 12 cities were categorized in this manner, 42 percent were lawn sites (maintained), while 58 percent were waste sites (not maintained). This difference was not considered significant. However, the second categorization showed that 70 percent of the PCB-positive sites were urban, or within the city limits, whereas only 30 percent were classified as suburban sites. In comparison, the ratio of urban to suburban sites for these 19 cities was 37 percent to 63 percent.

In summary, PCB occurrence in agricultural soils is extremely rare and is not considered a problem. However, the occurrence of these compounds is more prevalent in metropolitan areas, particularly within city limits, and monitoring should be continued to determine trends over time.

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Table 1. Occurrence of polychlorinated biphenyls in soils of five U.S. cities sampled in 1971. U.S. Environmental Protection Agency Urban Monitoring Program

Location	Total No. of sites	No. of positive detections	Percent of positive detections	Detected values (ppm) Minimum	Maximum	Arithmetic mean (ppm)	Geometric mean estimate (ppm)	PCB type-if identified
Baltimore, Md.	156	6	3.9	0.09	0.74	0.02	0.001	1260
Gadsden, Ala.	55	1	1.8	11.94		0.21	*[b]	not identified
Hartford, Conn.	48	ND[a]	-					
Macon, Ga.	43	ND	-					
Newport News, Va.	78	1	1.3	3.30		0.04	*	1254

[a] ND = Not detected.

[b] * = Geometric mean estimate not calculated when less than two positive values present.

Table 2. Occurrence of polychlorinated biphenyls in soils of five U.S. cities sampled in 1972. U.S. Environmental Protection Agency Urban Monitoring Program

Location	Total No. of sites	No. of positive detections	Percent of positive detections	Detected values (ppm) Minimum	Maximum	Arithmetic mean (ppm)	Geometric mean estimate (ppm)	PCB type-if identified
Des Moines, Iowa	82	3	3.7	0.34	0.94	0.03	0.002	not identified
Fitchburg, Mass.	35	ND[a]	-					
Lake Charles, La.	70	1	1.4	1.31		0.02	*[b]	1254
Pittsburgh, Pa.	189	1	0.5	1.01		0.01	*	not identified
Reading, Pa.	49	ND	-					

[a] ND = Not detected.

[b] * = Geometric mean estimate not calculated when less than two positive values present.

Table 3. Occurrence of polychlorinated biphenyls in soils of five U.S. cities sampled in 1973. U.S. Environmental Protection Agency Urban Monitoring Program

Location	Total No. of sites	No. of positive detections	Percent of positive detections	Detected values (ppm) Minimum	Maximum	Arithmetic mean (ppm)	Geometric mean estimate (ppm)	PCB type-if identified
Evansville, Ind.	82	ND[a]	-					
Greenville, S.C.	86	3	3.5	0.13	1.59	0.02	0.001	1254
Pittsfield, Mass.	45	ND	-					
Tacoma, Wash.	95	6	6.3	0.18	0.63	0.03	0.003	1-1254 5-not identified
Washington, D.C.	116	2	1.7	0.32	0.80	<0.01	0.001	1-1254 1-not identified

[a] ND = Not detected.

Table 4. Occurrence of polychlorinated biphenyls in soils of five U.S. cities sampled in 1974. U.S. Environmental Protection Agency Urban Monitoring Program

Location	Total No. of sites	No. of positive detections	Percent of positive detections	Detected values (ppm) Minimum	Maximum	Arithmetic mean (ppm)	Geometric mean estimate (ppm)	PCB type-if identified	Percent of Analyses Completed
Durham, N.C.	66	1	1.5	0.40		0.01	*[b]	1254	94
Gary, Ind.	89	5	5.6	0.50	3.33	<0.01	0.003	1-not identified 4-1254	100
San Francisco, Calif.	119	3	2.5	0.39	1.15	<0.01	0.001	1-not identified 1-1254 1-1260	71
Springfield, Ill.	72	ND[a]	-						100
Pine Bluff, Ark.	59	Analyses not completed							

[a] ND = Not detected.

[b] * = Geometric mean estimate not calculated when less than two positive values present.

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Persistence of Parathion in Soil

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Concern about persistence of synthetic pesticides in soil and the environment in general has been greater where chlorinated hydrocarbon compounds have been involved than where organophosphorus pesticides have been used. This is understandable, inasmuch as organophosphorus compounds generally degrade more rapidly in the environment. Most of the research concerning degradation or disappearance of organophosphorus compounds from soil has involved relatively low initial levels of pesticide resulting from conventional applications of the compounds for insect control. At these levels the degradation of organophosphorus compounds has generally been much more rapid than with chlorinated hydrocarbon compounds (1,2). Recently Stewart et al. (3) found traces of parathion in soil 16 years after the last application. The finding at this laboratory (4) that spillage of emulsifiable concentrate parathion and azinphosmethyl on soil at spray machine fill sites, air application flight strips, and other locations may be a hazard to children because of the presence of persistently high concentrations of the pesticides, has prompted our further investigation into the problem of persistence of organophosphorus compounds in soil. The purpose of the present study was to determine the disappearance of parathion residues in soil following topical applications of the compound. The results are intended to have application to problems related to waste pesticide disposal, of leaching, and of degradation or disappearance of parathion in the environment, as well as to the problem of hazard to children who may come in contact with contaminated spillage areas.

Materials and Methods

The experiment involved treatments of field soil plots using three liquid parathion concentrations and two different formulations. Treatments were: (a) undiluted commercial grade 45.6% liquid emulsifiable concentrate, (b) conventional dilute spray for orchard use prepared from water-wettable powder and containing 0.03% parathion (referred to as 1X concentration), (c) a dilute spray similar to (b) except prepared from emulsifiable concentrate, (d) a spray mixture of the type commonly used for semi-concentrate spray applications prepared from water-wettable powder and containing 0.24% parathion (8X--eight times the normal 1X

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concentration), and (e) a spray mixture similar to (d) except prepared from emulsifiable concentrate. The undiluted emulsifiable concentrate treatment was included in order to simulate spillage of concentrate pesticide and the more dilute concentrations were used because of the occasional practice of dumping various quantities of unused liquid spray formulation from spray machines onto the ground after finishing a particular spray operation. The undiluted emulsifiable concentrate and 8X treatments were replicated four times in each of three field plots. The 1X treatments were replicated four times in two field plots.

All experimental plots were subjected to the natural elements such as rainfall (average approximately 10 inches per year), sunlight (over 275 days during each year), and relatively high maximum temperatures (over 90°F for an average of 14 days each summer). The plots were covered with snow for approximately 2 months of each year. All three plots were sandy loam soil; however, plot 3 was on the verge of being classed as loamy sand. Plot 1 soil contained 11.2% clay, 34.2% silt, 54.6% sand, and 2.5% organic matter. The pH ranged from 4.4 to 5.4 with a mean of 4.7. This plot was subjected to sprinkler irrigation for a 24-hour period each 2 weeks during the summer season. The other two plots were not irrigated. Plot 2 soil contained 10.2% clay, 29.0% silt, 60.8% sand, and 3.4% organic matter. The pH ranged from 6.7 to 7.4 with a mean of 7.1. Plot 3 soil contained 6.0% clay, 26.0% silt, 67.3% sand, and 1.0% organic matter. The pH ranged from 6.6 to 7.8 with a mean of 7.3.

Metal frames 12-inches square were used to outline the individual soil test areas within each experimental plot. These were left in place for the duration of the experiment. The frames were pressed into the soil so that when 2 quarts of liquid parathion formulation were applied topically within the frame, a pool approximately 3/4-inch deep was formed before the material soaked into the soil. Samples of soil from two depths (0-1 in. and 1-3 in.) were taken 1 day following application and at intervals thereafter up to 5 years. At the 6th-year period two soil test areas were sacrificed and four replicate samples taken from each area at different depths in increments of 3 inches down to the 24-inch level.

Soil samples to the 3-inch level in all plots were taken by use of a cork borer tube which was cleaned after collection of each sample. Care was taken to minimize cross contamination between soil samples at different depths. However, it was difficult to avoid some cross contamination, due to limited surface area of test plots, especially after the 3rd year of sampling. It was felt that cross contamination of samples below the 3-inch depth was negligible because samples in this area were taken by

removal of entire layers of soil.

Parathion content of soil samples was determined in most cases by the method of Averell and Norris (5). In later years gas liquid chromatography was occasionally utilized as a check for accuracy and was used for analysis of deep soil samples where pesticide might be expected to be present in very low levels, if at all. This system was also used for analysis of paraoxon and other closely related alteration or breakdown products. Analysis for aminoparathion was by a modification of the Averell-Norris method and analysis for p-nitrophenol was by the method of Elliott et al. (6).

The effect of parathion on soil microorganisms was determined using number of colonies developed on nutrient yeast dextrose agar as an indicator. Soil innoculations at four different dilutions were made in 100 mm petri dishes containing the media. Because of the difficulty of accurately classifying the many different organisms found in soil they were divided into only two categories: filamentous and nonfilamentous.

Results and Discussion

As can be seen in Fig. 1, parathion persisted at relatively high levels for 5 years following gross topical contamination with the 45.6% emulsifiable concentrate formulation. The levels of pesticide in the soil, initially very high (30,000 to 95,000 ppm), were considerably lower by the end of the first year. By the second year the rate of disappearance was much less, with appreciable quantities remaining in both the top 1 inch and the 1- to 3-inch levels at the end of the 5th year. The lowest level found in a single sample at that time was 13,800 ppm (approximately 1.4%) parathion in the top 1 inch of soil. This level is higher than that involved in a near-fatal poisoning case where a child ingested soil from a contaminated area in a driveway near his home (7). In that incident the soil contained 8,634 ppm of parathion and was a result of spillage which had occurred at least 6 months prior to the incident.

There was no great difference in rate of disappearance of parathion among the three emulsifiable concentrate experimental plots. In individual plots more parathion was present in the top 1 inch of soil than in the 1- to 3-inch level for approximately 2 years; however, after that period the difference became much less. At 5 years some of the 3-inch depth samples contained more parathion than those from the 1-inch depth. At the 6-year period where soil was checked in increments of 3 inches down to the 24-inch level, very little parathion was found below the 9-inch level (see Table 1).

At the 4th-year period following application two emulsifiable concentrate plots were checked for presence of parathion alteration products in the top 3 inches of soil. Where parathion content of soil ranged from 16,662 to 26,746 ppm the amount of p-nitrophenol found ranged from 11.2 to 41.0 ppm. No aminoparathion, paraoxon or S-ethyl parathion could be detected. The inability to find aminoparathion was expected because of the great instability of the compound. Instrumentation available at the time the samples were analyzed was not adequate to properly identify and quantitate paraoxon and S-ethyl parathion. However, a recent recheck of the sample extracts by improved methods has indicated the presence of small amounts of paraoxon and S-ethyl parathion. Improved instrumental capability in recent years has allowed additional studies at this laboratory on parathion alteration products in soil which will be reported at a later date.

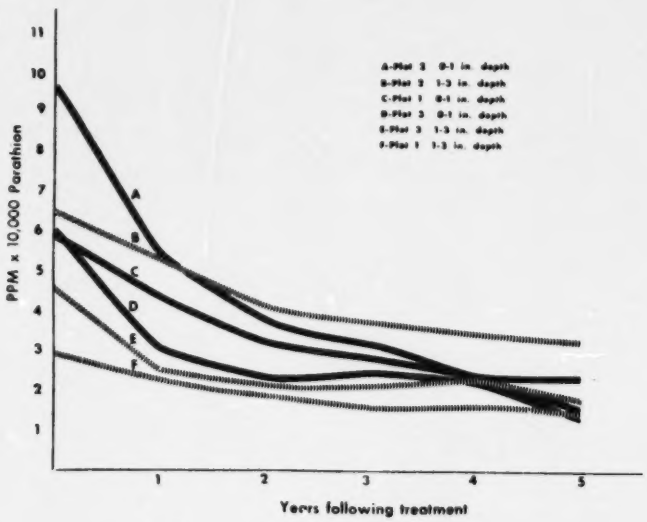

Figure 1. Disappearance of parathion from sandy loam soil, following gross topical contamination with emulsifiable concentrate formulation (45.6%), at two depths in three experimental plots. Each value average of 4 replicates.

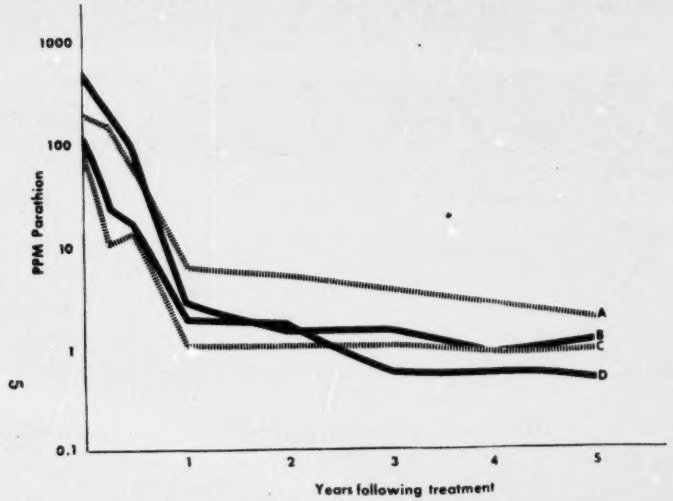

Figure 2. Disappearance of parathion from top 1 inch of sandy loam soil following topical applications of two concentrations using two formulations. A = 8X (0.24%) and C = 1X (0.03%) sprays using water-wettable powder formulation. B = 8X (0.24%) and D = 1X (0.03%) sprays using emulsifiable concentrate formulation. A and B average of 12 replicates and C and D average of 8 replicates.

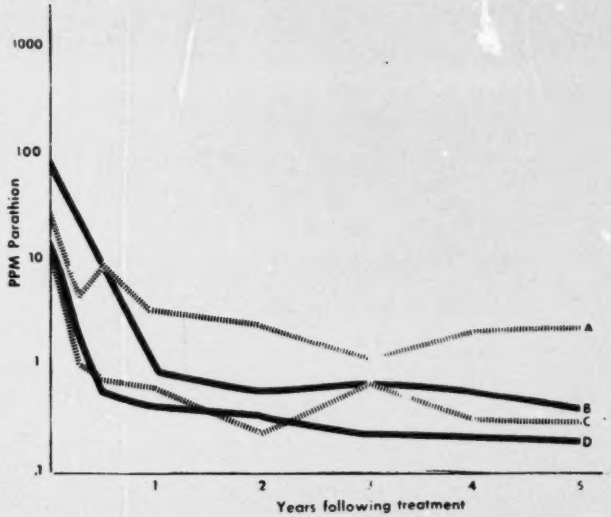

Figure 3. Disappearance of parathion from 1- to 3-inch depth of sandy loam soil following topical applications of two concentrations, using two formulations. A = 8X (0.24%) and C = 1X (0.03%) sprays using water-wettable powder formulation. B = 8X (0.24%) and D = 1X (0.03%) sprays using emulsifiable concentrate formulation. A and B average of 12 replicates and C and D average of 8 replicates.

TABLE 1

Parathion in Soil at Different Depths Six Years After Topical Application of Emulsifiable Concentrate Formulation (45.6%).

Depth (inches)	PPM Parathion*	
	Plot 1	Plot 2
0-1	14,500	15,370
1-3	14,900	9,330
3-6	9,900	9.65
6-9	149.4	9.48
9-12	0.004	0.097
12-15	0.048	0.008
15-18	0.004	0.017
18-21	0.011	el**
21-24	el**	el**

*Average of 4 replicates.

**Below lower limit of sensitivity of method (< 0.002 ppm)

Figures 2 and 3 show persistence of parathion at two depths in soil plots where the more dilute liquid spray concentrations were applied topically. There was very little difference in values obtained among these experimental plots; therefore, average values for replicates in the three plots were used in plotting the curves. As with the more concentrate applications discussed above, the levels of parathion in soil dropped off quite rapidly during the first year with a trend toward leveling off thereafter. Where the 1X (0.03%) concentration was applied, average levels after 5 years were from 0.6 to 1.2 ppm in the top 1 inch of soil and from 0.2 to 0.3 ppm in the 1- to 3-inch depth. Where the 8X (0.24%) concentration was applied, average levels after 5 years were 0.4 to 1.5 ppm in the top 1 inch of soil and from 1.2 to 3.6 ppm in the 1- to 3-inch level. It appears that slightly higher levels of pesticide remained in the soil after 5 years where water-wettable formulation was used than where the emulsifiable was used. Two sets of the experimental plots will be retained so that samples can be analyzed after much longer periods of time than 5 years. By using more sensitive methods, perhaps any differences at low levels can then be more clearly defined.

On finding relatively high levels of parathion in the top 3 inches of soil in the concentrate plots at the end of the 2-year period, we decided to determine if soil microorganisms were being appreciably affected. Soil isolations at four different dilutions were made on yeast-dextrose agar. Counts of the number of colonies that had developed in 6 days at 70°F were used as an indicator. As can be seen in Table 2, under the conditions of our experiment, fewer colonies were isolated from the concentrate parathion soil plot than from untreated control soil nearby. Also, when untreated control soil inoculum was placed in media containing 0.5% parathion the counts were considerably lower, and where the media contained 5.0% parathion the microorganism colony development was almost completely inhibited. Where the inoculum was from a plot treated with parathion 2 years earlier, and containing approximately 3.4% parathion, there was also similar reduction in the media containing 0.5% parathion, indicating that there had been no appreciable development of resistance to the pesticide by the organisms as indicated by the methods used in the test.

Table 3 shows results of inoculations of soil taken from another concentrate parathion plot at the 5th year following topical application with the pesticide. This is compared with untreated control soil inoculum taken nearby. In this experimental plot area the counts for the untreated control area were

TABLE 3

Effect of Parathion on Soil Microorganisms Expressed as Colony Numbers on Nutrient Yeast-Dextrose Agar Following Soil Isolations.

Sample	Culture Dilution in H_2O	Number of Colonies Developed in 6 Days at 70°F[a]	
		Nonfilamentous	Filamentous
1[b]	1-1000	2500.0	1000.0
	1-10,000	817.3	477.0
	1-100,000	181.0	100.3
	1-1,000,000	57.0	24.3
2[c]	1-1000	89.0	18.6
	1-10,000	21.3	4.6
	1-100,000	5.6	0.6
	1-1,000,000	2.6	1.0

[a] Each value is average of counts observed on three 100 mm petri dishes. Sampled from top 1 inch of soil.
[b] Untreated control soil near treated plots.
[c] Soil 5 years after topical application with 45.5% emulsifiable concentrate. Approximately 2.9% parathion at time of sampling.

TABLE 2

Effect of Parathion on Soil Microorganisms Expressed as Colony Numbers on Nutrient Yeast-Dextrose Agar Containing Different Levels of Parathion as an Indicator.

Media	Culture Dilution in H_2O	Number of Colonies Developed in 6 Days at 70°F[a]			
		Soil from Control Plot Containing no Parathion		Soil from Test Plot Containing approx. 3.4% Parathion[b]	
		Nonfilamentous	Filamentous	Nonfilamentous	Filamentous
A:					
Contained	1-1000	< 200.0	10.0	106.0	0.0
no	1-10,000	83.0	6.7	26.7	0.0
Parathion	1-100,000	61.7	9.0	3.7	0.0
	1-1,000,000	24.7	4.7	4.3	0.3
B:					
Contained	1-1000	40.3	2.3	6.3	0.0
0.5%	1-10,000	2.3	0.7	4.7	0.0
Parathion	1-100,000	0.7	0.0	0.0	0.0
	1-1,000,000	0.7	0.0	0.0	0.0
C:					
Contained	1-1000	0.0	2.0	0.0	0.0
5.0%	1-10,000	0.0	0.0	0.0	0.0
Parathion	1-100,000	0.0	0.0	0.0	0.0
	1-1,000,000	0.0	0.0	0.0	0.0

[a] Each value is average of counts observed on three 100 mm petri dishes. Sampled from top one inch of soil.

[b] Topical application of 45.5% emulsifiable concentrate parathion 2 years earlier. Innoculum from this plot included to determine if any microorganisms subjected to parathion in soil for a two-year period had developed a detectable resistance to the pesticide.

also considerably higher than those for the treated plot. Counts for the plot treated with parathion 5 years earlier were much lower than the control, indicating that growth of micro-organisms was still being inhibited to some extent after this period of time.

It should be pointed out that the counts shown in Tables 2 and 3 are not comparable since isolations were made in different years and at different times of the year.

In the above studies disappearance of parathion from soil occurred at a much slower rate than one might have expected, considering the year-around exposure to the natural elements. This was especially true in the experimental plots where the highly concentrated formulation was involved.

Many factors undoubtedly affected the disappearance of parathion from the soil, such as adsorption onto soil particles, volatilization, leaching, photochemical decomposition, chemical decomposition, and microbiological degradation, to name a few. Under conditions of this study adsorption undoubtedly played an important role. Leaching apparently was minimal. We did not attempt to determine loss from volatilization.

Findings reported in the present paper emphasize that when a high concentration of parathion is present as a result of spillage on soil it may persist for a long period of time and thus should be dug up and disposed where it will not be a hazard to small children or animals, and will not be available on the surface to contaminate the environment.

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SPILLAGE OF PESTICIDES AND RESIDUES IN SOIL*

by H. R. WOLFE and W. F. DURHAM

Here in the orchard areas of central Washington we are living in an area which has one of the highest rates of pesticide usage of any area in the United States. The fact that there has been a good safety record in central Washington in relation to the use of hazardous pesticides speaks well for present methods of handling and applying pesticides. However, to maintain this good safety record we must constantly be aware of the potential hazards where toxic pesticides are being used.

In recent years, emphasis has been placed in presentations before this Association on the hazard of pesticides to spraymen and other agricultural workers and on the danger of improper disposal of supposedly empty pesticide containers (1). An additional factor in the safe use of pesticides which should be emphasized involves spillage of pesticides (either use formulations or, particularly, concentrates) and the resulting residues in soil.

The hazard of such a spillage was emphasized by a recent near-fatal poisoning case (5). This incident resulted from a child ingesting soil from a driveway near his home where concentrated liquid parathion had dripped on to the ground from his father's truck, resulting in an oily-appearing area not unlike that normally found in driveways as a result of oil leakage from vehicles. Chemical analysis of the soil showed it to contain 8,634 ppm parathion. Upon investigation it was found that the soil had been contaminated at least six months before the child ingested the dirt and became seriously ill.

In addition to the danger to children playing in or eating these concentrated residues, there is also a possible health hazard from food crops grown in highly contaminated soil.

Although it is a well-known fact that chlorinated hydrocarbon pesticides such as DDT, aldrin, dieldrin, heptachlor, and chlordane, to name only a few, are very persistent in soil (2,3,4), the rapid hydrolysis or decay of the organic phosphorus compounds, such as parathion and azinphosmethyl (Guthion), on exposure to the elements, such as rain, sunshine, and high temperatures, would seem to make them relatively less important as environmental contaminants. However, the persistence of the parathion leading to the above-mentioned poisoning incident indicates that organic phosphorus pesticides, especially where spillage of a large quantity of concentrated material occurs, do not break down as rapidly as might be expected.

A study was carried out to determine the initial amount and persistence of parathion and azinphosmethyl residues in soil resulting from contamination with various formulations of the insecticides. Replicated tests were set up to simulate spillage of undiluted emulsifiable concentrate material (45.6% parathion and 18.1% azinphosmethyl). Azinphosmethyl, due to its low dermal toxicity, is considered less hazardous to use in orchard spraying than parathion; however, it is almost as toxic as parathion when taken orally. Although very little emulsifiable form of azinphosmethyl is used in the orchard areas of central Washington, this formulation was included for comparison with parathion. Other tests included contamination of soil by simulating tank drainage onto the ground with conventional dilute (1x) and concentrate (8x) liquid sprays using both wettable powder and emulsifiable concentrate formulations of both compounds. Test plots were in orchard silt-loam soil with high organic material content and a pH ranging from 4.4 to 5.5 with a mean of about 5.0. The plots were in an orchard and exposed to weathering and to regular sprinkler irrigation.

Results of the parathion study showed that the top one-inch of soil contaminated with emulsifiable concentrate contained a large amount of the compound initially (59,000 ppm or 5.9%). This residue showed only moderate decay (about 46%) over a two-year test period. With the more dilute formulations the mean initial surface-soil concentrations varied from 98 to 108 ppm with the 1x spray and from 370 to 1,126 ppm with the 8x mixture.

Surface soil contaminated with emulsifiable concentrate azinphosmethyl also

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Important discussion for plan in handling and safety measures

contained a large amount of the compound initially (29,000 ppm or 2.9%). The decay of this material was only about 10% over a two-year period. With the more dilute formulations the mean initial soil concentrations varied from 193 to 278 pm with the 1x spray and from 1,904 to 2,337 ppm with the 8x mixture.

There was little difference between the more dilute formulations of parathion and azinphosmethyl prepared from wettable powder and those from emulsifiable concentrate either with respect to initial deposit or to persistence. All varieties of dilute spray formulations decayed more rapidly than did the undiluted emulsifiable concentrate. After two years all mean values for the more dilute formulations of both compounds were below 100 ppm.

Samples taken at a site where dilute (1x) parathion spray was shown to have been drained from a spray tank one month earlier showed 91 ppm in the top one-inch of the soil. Analysis of samples from a site where concentrate (8x) azinphosmethyl spray was known to have been drained from a spray machine six months earlier showed 1,333 ppm of the pesticide in the top one-inch of the soil.

Topsoil samples from 37 spray-machine fill sites taken at random in the Wenatchee Valley area showed no level of parathion or azinphosmethyl as high as that present initially in the emulsifiable concentrate experimental plots. The time between contamination of soil and taking of these samples for analysis is not known, however. Parathion values ranged from 0.3 to 330 ppm with a mean of 48.4 ppm. Azinphosmethyl values ranged from 0.4 to 8,428 ppm with a mean of 1,351 ppm. It is interesting to note that the high value found for azinphosmethyl (8,428 ppm) is near that found for parathion (8,634 ppm) in the soil ingested by the severely poisoned child mentioned earlier in this paper.

It is evident from the data presented that organic phosphorus compounds such as parathion and azinphosmethyl may persist in the soil at relatively high levels for long periods of time. This is especially true where highly concentrated forms of the pesticide materials are spilled on the soil. Such spillage is a potential hazard to small children, as in the poisoning case described above, and might contaminate food crops, particularly root vegetables, grown in the soil.

Extreme caution should be exercised in pouring or measuring concentrate pesticides to see that none is spilled. Measuring, mixing, and filling for spray operations should be done in areas away from homes, schools, or other places frequented by children. If there is significant spillage, particularly around dwellings or other inhabited areas, the contaminated soil should be dug out and buried in a safe location.

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